Statistical Foundations of Wave-Mechanics

by
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Summary:

It is shown that Schrödinger's time-independent equation can be derived from Boltzmann's statistics, if the discontinuities necessarily existing in the latter theory are taken into account. Moreover, a proof is given that Schrödinger's time-dependent equation can also be obtained from Boltzmann's statistics, if a simple statistical assumption concerning the dependence of density in phase space on energy and time is introduced.

Introduction: The need for a rational foundation of wave-mechanics

It is well-known that Einstein showed a sceptical attitude towards the Copenhagen interpretation of quantum mechanics. He favoured a statistical point of view in place of the dualistic one. In 1949, in a volume celebrating his 70th birthday, Einstein made the following most interesting remark[1]:

"Assuming the success of efforts to accomplish a complete physical description, the statistical quantum theory would, within the framework of future physics, take an approximately analogous position to the statistical mechanics within the framework of classical mechanics. I am rather firmly convinced that the development of theoretical physics will be of this type; but the path will be lengthy and difficult."

Ideas similar to Einstein's have also been propounded by Alfred Landé, who, during the last two decades, constantly demanded for a revision of duality, uncertainty and complementarity in favour of a corpuscular-statistical quantum theory. In 1961 he wrote[2]:

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1) Albert Einstein: Philosopher-Scientist. The Library of Living Philosophers. Ed. Paul Arthur Schilpp. New York, 2nd ed. 195 See: Remarks concerning the essays brought together in this co-operative volume, pp. 665-688; especially p. 672.

2) Alfred Landé, Warum interferieren die Wahrscheinlichkeiten? Zeitschrift für Physik, Vol. 162, 1961, pp. 410-412.

"What we need as an explanation is a reduction of the strange wave-like rules of particle mechanics to simple and plausible non-undulatory principles";

and in 1969 he suggested that[3] "a way out of the labyrinth of contradictory interpretations will be to deduce the formalism of quantum theory from elementary postulates which should be absolutely clear and devoid of quantum features to avoid circularity."

In 1967, Sir Karl Popper, in an impressive defence of the statistical nature of quantum-mechanics, set out as follows[4]:

"My first thesis concerns the most important thing for understanding quantum theory: the kind of problems which the theory is supposed to solve. These, I assert, are essentially statistical problems."

Then, commenting on his second thesis ("statistical questions demand, essentially, statistical answers"), Popper added:

"Statistical conclusions cannot be obtained without statistical premisses. And therefore answers to statistical questions cannot be obtained without a statistical theory."

Indeed, a number of urgent questions arises upon studying usual presentations of quantum mechanics, namely:

1) The equations of wave-mechanics are subject to a statistical interpretation. Is it possible also to give statistical reasons for this interpretation?
2) The comparison with the experiments requires the transition from the ψ-function of the time-independent Schrödinger equation to its square. Is there any reason why ψ^2 is theoretically as justified as ψ ?
3) What is the physical meaning of the mathematical connection between the time-dependent and the time-independent Schrödinger-equation?

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3) idem, Wahrheit und Dichtung in der Quantentheorie. Physikalische Blätter, 25. Jg, 1969, pp. 105-109.
4) Karl R. Popper, Quantum Mechanics Without "The Observer". Quantum Theory and Reality. Ed. Mario Bunge. Berlin, Göttingen, Heidelberg, New York 1967. Studies in the Foundations, Methodology, and Philosophy of Science. Vol. 2, pp. 7-44; especially p. 15.

4) Why does the imaginary unit i enter the time-dependent Schrödinger-equation?

Neither Schrödinger's original version of wave-mechanics which presented the latter as an expansion of Newton's mechanics on account of an analogy between optics and mechanics, nor the axiomatizations of quantum mechanics answer the foregoing questions. In Schrödinger's approach at least the time-dependent equation enters the scene like a deus ex machina. The same is true with the usual axiomatizations which begin quantum mechanics by postulating the time-dependent equation. Here the advantage of apparent mathematical rigo~~resity~~ is more than counterbalanced by the disadvantage that the foregoing physical questions remain open. Now, any foundations whatsoever will rest upon principles of an axiomatic character. Therefore, the last question to be raised here is:

5) Can there be given simpler axioms, so that the replies to our questions appear as natural consequences of our physical assumptions?

In the course of a study of the historical development of quantum theory, especially of the period ranging from Boltzmann to Planck[5], I have lately been led to the same convictions as Einstein, Landé, and Popper. For Planck's discovery of the quantum of action and his derivation of the law of black-body radiation were based on Boltzmann's statistical considerations[6], so that the quantum theory from its outset had strong statistical features. Later, Max Born, after an ~~episode~~ interval of almost thirty years, gave wave-mechanics a statistical interpretation. Therefore I think that it is worthwhile to look for the statistical foundations of wave-mechanics, and I am convinced that the problem will be brought nearer to a solution (if it is not solved at all), if it proves possible to deduce Schrödinger's equations

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5) Ulrich Hoyer, Von Boltzmann zu Planck. In print in: Archive for History of Exact Sciences.
6) Thomas S. Kuhn, Black-Body Theory and the Quantum Discontinuity 1894-1912, Oxford, New York 1978.

from probabilistic or statistical assumptions as required by Landé and Popper.

The possibility of a statistical derivation of the quantum theory has already been discussed by Fényes[7] and Bopp[8]. However, in contradistinction to Fényes, who thought that statistical mechanics cannot be applied to wave-mechanics, Schrödinger's theory will be derived here from ideas very similar to Boltzmann's statistical considerations. Bopp, on the other hand, emphasized that Newtonian mechanics is of no use in quantum theory, whereas the deduction given here will be based on classical mechanics (at least indirectly, as Boltzmann's considerations which rest upon the classical expressions for total energies are made the point of departure).

Incidentally, the following derivation differs also from the stochastic attempts made in recent years.[9] Firstly, I make fewer assumptions. Secondly, the stationary case will be considered first, while the time-dependent equation will be derived afterwards, in contradistinction to the stochastic procedure of, say, J.C. Aron.

Finally, I wish to add that I take a line of reasoning which in the beginning follows closely a paper published by Ludwig Boltzmann in 1877 under the title "On the relation of the second law of the mechanical theory of heat and of the theory of probability to the theorems on the equilibrium of heat."[10]

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7) Imre Fényes, Eine wahrscheinlichkeitstheoretische Begründung und Interpretation der Quantenmechanik. Zeitschrift für Physik, Vol. 132, 1952, S. 81-1o6.

8) Fritz Bopp, Korpuskularstatistische Begründung der Quantenmechanik. Zeitschrift für Naturforschung, Vol. 9a, 1954, pp. 579-6oo.
idem, Statistische Mechanik bei Störung des Zustandes eines physikalischen Systems durch die Beobachtung. Werner Heisenberg und die Physik unserer Zeit. Braunschweig 1961, pp. 128-149.

9) J.C. Aron, A Stochastic Basis for Microphysics. Foundations of Physics, Vol. 9, 1979, pp. 163-191.

1o) Ludwig Boltzmann, Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung respektive den Sätzen über das Wärmegleichgewicht. Wissenschaftliche Abhandlungen, Vol. 2, reprint of the first edition Leipzig 19o9, New York 1968, pp. 164-223.

Boltzmann statistics of the one electron system

Consider a physical system, e.g. a gas, consisting of a large number n of atoms enclosed in a certain volume. The atoms are composed of nuclei and electrons. In order not to complicate the following formulae too much we first study the simplest case, namely that in which every atom contains one single electron. In the stationary state the velocities of the atoms will be distributed according to Maxwell's law. However, the following considerations do not refer to a laboratory system but to systems of coordinates parallel to each other with their origins in the centres of gravity of the atoms, i.e. approximately in the nuclei. For statistical reasons these coordinate systems and the appertaining velocity systems are divided into a large number of elements of finite extension $\Delta x = \Delta y = \Delta z = \varepsilon$ and $\Delta \dot{x} = \Delta \dot{y} = \Delta \dot{z} = \eta$. We now ask for the most probable distribution of a given constant amount of energy U among the n electrons present in the atoms. To this purpose we introduce the following statistical axiom, which led Boltzmann to the discovery of the relation of entropy and probability:

Each special distribution ("Komplexion" in Boltzmann's terms) of the electrons over the cells of the 6n- dimensional phase space, which is compatible with energy conservation, is as probable as any other.

If the number of electrons present in a certain element of 6-dimensional phase space μ with coordinates $x = a \Delta x$, $y = b \Delta y$, $z = c \Delta z$, $\dot{x} = \dot{a} \Delta \dot{x}$, $\dot{y} = \dot{b} \Delta \dot{y}$, $\dot{z} = \dot{c} \Delta \dot{z}$ is $\omega_{abc\dot{a}\dot{b}\dot{c}}$, then the density of electrons in phase space μ, f, is

$$f(a\Delta x, b\Delta y, c\Delta z, \dot{a}\Delta\dot{x}, \dot{b}\Delta\dot{y}, \dot{c}\Delta\dot{z}) = \frac{\omega_{abc\dot{a}\dot{b}\dot{c}}}{\Delta x \Delta y \Delta z \Delta \dot{x} \Delta \dot{y} \Delta \dot{z}} .$$

The number of permutations P to which a certain distribution, characterized by definite values of $\omega_{abc\dot{a}\dot{b}\dot{c}}$, is subject, will be

$$(1)\quad P = \frac{n!}{\prod_{a=-p}^{a=+p}\prod_{b=-q}^{b=+q}\prod_{c=-r}^{c=+r}\prod_{a'=-p'}^{a'=+p'}\prod_{b'=-q'}^{b'=+q'}\prod_{c'=-r'}^{c'=+r'} \omega_{abca'b'c'}!}$$

Because of conservation of energy we here assume that $x, y, z, \dot{x}, \dot{y}$, and $\dot{z}$ vary from $-p$ to $+p$, $-q$ to $+q$ etc. with finite values of p, q, r, p', q', and r'. However, neither the finiteness in geometrical space nor the symmetry with respect to the limits $-p$ and $+p$ etc. are necessary for our calculation and can be given up in special cases.

According to Boltzmann the stationary state is the most probable one and therefore characterized by the maximum of P. Instead of maximizing P we look for the maximum of ln P. Furthermore, the number of atoms n should be large enough to ensure that the factors $\omega_{abca'b'c'}!$ in equation (1) can be replaced by Stirling's formula

$$\omega_{abca'b'c'}! = \sqrt{2\pi}\left(\frac{\omega_{abca'b'c'}}{e}\right)^{\omega_{abca'b'c'}}$$

Then the most probable distribution will be given by the maximum of

$$\ln P = n \ln n - (p+q+r+p'+q'+r'+1)\ln 2\pi$$

$$(2)\quad -\sum_{a=-p}^{a=+p}\sum_{b=-q}^{b=+q}\sum_{c=-r}^{c=+r}\sum_{a'=-p'}^{a'=+p'}\sum_{b'=-q'}^{b'=+q'}\sum_{c'=-r'}^{c'=+r'} \omega_{abca'b'c'} \ln \omega_{abca'b'c'}.$$

In place of (2) we write

$$\ln P = n \ln n - (p+q+r+p'+q'+r'+1)\ln 2\pi - n \ln(\Delta x \Delta y \Delta z \Delta \dot{x} \Delta \dot{y} \Delta \dot{z})$$

$$(3)\quad -\sum\sum\sum\sum\sum\sum f \ln f \cdot \Delta x \Delta y \Delta z \Delta \dot{x} \Delta \dot{y} \Delta \dot{z}.$$

Obviously, each element Δx , Δy, Δz, $\Delta \dot{x}$, $\Delta \dot{y}$, $\Delta \dot{z}$ must be finite, for otherwise the second term of the sum (3), and possibly the third term as well, would increase infinitely. In this case, however, the calculation of the maximum intended here would make no sense. Moreover, we must keep in mind that the maximum will be determined under the additional conditions that the number of particles and also their energy be conserved:

$$(4) \qquad n = \sum\sum\sum\sum\sum\sum f \, \Delta x \, \Delta y \, \Delta z \, \Delta \dot{x} \, \Delta \dot{y} \, \Delta \dot{z} \quad ,$$

and

$$(5) \qquad \mathcal{U} = \sum\sum\sum\sum\sum\sum \left(V + \frac{m}{2}\left[(a' \Delta \dot{x})^2 + (b' \Delta \dot{y})^2 + (c' \Delta \dot{z})^2 \right] \right) \times f \, \Delta x \, \Delta y \, \Delta z \, \Delta \dot{x} \, \Delta \dot{y} \, \Delta \dot{z} \quad .$$

Here m is the (reduced) mass of the electron. Maximizing equation (3) under the conditions (4) and (5) is a problem in the calculus of variations, which can be solved by Lagrange's method of multipliers. The result is the well-known Maxwell-Boltzmann distribution

$$(6) \qquad f(a\Delta x, b\Delta y, c\Delta z, a'\Delta \dot{x}, b'\Delta \dot{y}, c'\Delta \dot{z}) = A e^{-\alpha \left\{ V(a\Delta x, b\Delta y, c\Delta z) + \frac{m}{2}\left[(a'\Delta \dot{x})^2 + (b'\Delta \dot{y})^2 + (c'\Delta \dot{z})^2 \right] \right\}} \quad ,$$

where α and A are positive constants $\neq 0$.

The distribution function (6) is discontinuous. It will now be replaced by a continuous function, namely

$$(7) \qquad f(x, y, z, \dot{x}, \dot{y}, \dot{z}) = A e^{-\alpha \left[V(x,y,z) + \frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \right]}$$

From the continuous Maxwell-Boltzmann distribution (7)

we obtain by partial differentiation applied to the velocity component $\dot{x}$

$$(8) \qquad \frac{\partial^2 f}{\partial \dot{x}^2} = f \alpha^2 m^2 \dot{x}^2 - \alpha m f \,.$$

Corresponding equations obtain for the components $\dot{y}$ and $\dot{z}$. Therefore, the kinetic energy in the element $a' \Delta \dot{x}, b' \Delta \dot{y}, c' \Delta \dot{z}$ of velocity space can be expressed by

$$(9) \qquad \frac{m}{2}\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right) f = \frac{1}{2\alpha^2 m}\left(\frac{\partial^2 f}{\partial \dot{x}^2} + \frac{\partial^2 f}{\partial \dot{y}^2} + \frac{\partial^2 f}{\partial \dot{z}^2} + 3\alpha m f\right).$$

The total energy Ef within the element of phase space $a \Delta x$, $b \Delta y$, $c \Delta z$, $a' \Delta \dot{x}$, $b' \Delta \dot{y}$, $c' \Delta \dot{z}$ then is

$$(10) \qquad f V + \frac{1}{2\alpha^2 m}\left(\frac{\partial^2 f}{\partial \dot{x}^2} + \frac{\partial^2 f}{\partial \dot{y}^2} + \frac{\partial^2 f}{\partial \dot{z}^2} + 3\alpha m f\right) = E f \,.$$

Since the potential V contains an arbitrary additive constant, equation (1o) can be transformed into

$$(11) \qquad f V + \frac{1}{2\alpha^2 m}\left(\frac{\partial^2 f}{\partial \dot{x}^2} + \frac{\partial^2 f}{\partial \dot{y}^2} + \frac{\partial^2 f}{\partial \dot{z}^2}\right) = E f \,.$$

Equation (11) is formally similar to the time-independent Schrödinger-equation, although the density function f - contrary to the space-dependent ψ-function - depends on six variables.

The correspondence of Boltzmann statistics and wave-mechanics

From equation (7) follows

$$(12) \qquad \frac{\partial^2 f}{\partial x^2} = \alpha^2 f \left(\frac{\partial V}{\partial x}\right)^2 - \alpha f \frac{\partial^2 V}{\partial x^2} \,.$$

Corresponding equations obtain for the variables y and z. We now calculate the second partial derivatives of f at those points in phase space for which the energy is constant:

$$(13) \qquad \frac{m}{2}\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right) + V = E = \text{const.}$$

Then equation (8) yields

$$(14)\quad \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} = 2\alpha^2 m f (E-V) - 3\alpha m f .$$

We now introduce the sum

$$(15)\quad P' = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} + \frac{1}{\sigma^2}\left(\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \right),$$

where σ is a certain constant to be determined later.
Equations (12) and (14) yield

$$P' = f \left\{ \alpha^2 \left[\left(\frac{\partial V}{\partial x}\right)^2 + \left(\frac{\partial V}{\partial y}\right)^2 + \left(\frac{\partial V}{\partial z}\right)^2 \right] - \alpha \left(\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} \right.\right.$$

$$(16)\qquad \left.\left. + \frac{\partial^2 V}{\partial z^2} \right) + \frac{1}{\sigma^2} \left[2 m \alpha^2 (E-V) - 3\alpha m \right] \right\} .$$

We now consider the <u>special</u> case of an isotropic, harmonic os= cillator in space having the potential function

$$(17)\qquad V = \frac{1}{2} \lambda \left(x^2 + y^2 + z^2 \right) + C$$

with λ and C constants.
Insertion in (16) yields

$$(18)\quad P' = f \alpha^2 \left[2\lambda V - 3\frac{\lambda}{\alpha} + \frac{m}{\sigma^2} \left(2E - 2V - \frac{3}{\alpha} \right) - 2\lambda C \right].$$

If we put

$$(19)\qquad \sigma^2 = \frac{m}{\lambda}$$

then

$$(20)\qquad P' = f \alpha^2 2\lambda \left(-\frac{3}{\alpha} + E - C \right) .$$

Insertion of (15) and (20) in (11) yields

$$(21)\quad Vf - \frac{\sigma^2}{2\alpha^2 m}\left(\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2}\right) = \left(C + \frac{3}{\alpha}\right) f.$$

Here the energy E has vanished from the equation. We now put

$$(22)\quad C + \frac{3}{\alpha} = E^*$$

and, dividing by the number of electrons n, we obtain

$$(23)\quad V\varphi - \frac{\sigma^2}{2\alpha^2 m}\left(\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2}\right) = E^* \varphi.$$

φ is the density of probability that an electron will be found at point $x,y,z,\dot{x},\dot{y},\dot{z}$ in phase space. Equation (7) shows that the functions f and φ contain a space- and a velocity-dependent factor

$$(24)\quad \varphi = \frac{f}{n} = \frac{g(x,y,z)\, g(\dot{x},\dot{y},\dot{z})}{n} = \psi(x,y,z)\, g(\dot{x},\dot{y},\dot{z}).$$

Division of equation (23) by the velocity dependent term g yields

$$(25)\quad V\psi - \frac{\sigma^2}{2\alpha^2 m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}\right) = E^* \psi.$$

If we here assume

$$(26)\quad K = \frac{\sigma}{\alpha} = \hbar \quad ,$$

equation (26) is analogous to the time-independent Schrödinger equation. The difference is, that according to equation (22) E^* is a constant, since α and C are assumed to be constants. Boltzmann statistics therefore yields the same result for the density of probability as wave-mechanics for the state of quantum number n=0. However, this remarkable correspondence of Boltzmann statistics and wave-mechanics ceases, as is obvious from equation (16), if we regard more complicated potential functions beyond the harmonic oscillator.

The time-independent Schrödinger equation for the one electron system

Now, it can be shown that Planck's theory of black-body radiation can be derived completely from Boltzmann's statistical assumptions[11]. More especially, the discontinuum of energies of harmonical oscillators then follows from the discontinuous division into cells of the phase space, which is necessary for our statistical treatment. Therefore, we suspect that there has been overlooked a fundamental property in the considerations hitherto presented. This cardinal point is the discontinuous character of the Maxwell-Boltzmann distribution. We duly stressed discontinuity in deriving equation (6); but in passing over to the derivation of the continuous equations (7), (8), and (11) we neglected these discontinuities. Therefore, in the following considerations we will take into account the discontinuities essentially inherent to the arising from statistical approach in passing over to continuous distribution functions.

First, the square of velocity in each lattice point of phase space is given by equation (8) with sufficient exactness, provided that the finite intervals in phase space are small enough, while the number of atoms is sufficiently large. Consequently, we demand from the continuous distribution in question that it will fulfil equation (11). On the other hand, we must take regard to the fact that the density is constant in the neighbourhood of any lattice point (f does not vary within each finite element in phase space!). Thus,

$$\underline{f} = \text{const.} \quad , \tag{27}$$

whence

$$\text{grad } f = 0 \quad , \tag{28}$$

and

$$\text{div grad } f = 0 \quad . \tag{29}$$

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11) see footnote 5).
and Einstein 1905

Trivially!

Hence, f obeys the potential equation in phase space. For dimensional reasons the velocity variables $\dot{x}$,$\dot{y}$, and $\dot{z}$ will now be multiplied by the unit of time τ, and the different terms of the potential equation become equal with respect to physical dimension without changing the numerical value

$$(30)\quad \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} + \frac{1}{\tau^2}\left(\frac{\partial^2 f}{\partial \dot{x}^2} + \frac{\partial^2 f}{\partial \dot{y}^2} + \frac{\partial^2 f}{\partial \dot{z}^2} \right) = 0 .$$

Insertion of (30) in (11) yields

$$(31)\quad Vf - \frac{\kappa^2}{2m}\left(\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \right) = E f .$$

with

$$(32)\quad \kappa = \frac{\tau}{\alpha} .$$

We next consider all points in phase space for which

$$(33)\quad E = \text{const.}$$

Then equation (29) also holds in passing from element to element in phase space. Moreover, f then depends on five independent variables, e.g. x,y,z,$\dot{x}$, and $\dot{y}$, so that

$$(34)\quad f = f(x,y,z,\dot{x},\dot{y}) .$$

If we put

$$(35)\quad \dot{x} = \text{const.} \quad , \quad \dot{y} = \text{const.} \quad ,$$

we obtain the same equation for the electron density in geometrical space for any pair of independent velocity coordinates (35). Therefore, we are allowed to omit the velocity variables in equation (31)

$$(36)\quad V f(x,y,z) - \frac{\kappa^2}{2m} \nabla^2 f(x,y,z) = E f(x,y,z) .$$

If we divide by the number of electrons n,

$$(37)\quad \psi = \psi(x,y,z) = \frac{f(x,y,z)}{n} ,$$

we obtain the following differential equation for the density of probability in geometrical space

$$(38)\quad V\psi - \frac{\kappa^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = E\psi .$$

This is the time-independent Schrödinger equation for the one electron system, apart from the numerical factor κ, which is as yet unknown and remains to be determined by experiment. Given the abbreviation

$$(39)\quad H\psi = V\psi - \frac{\kappa^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) ,$$

we finally obtain the well-known equation

$$(40)\quad H\psi = E\psi .$$

The time-independent Schrödinger equation for systems of several electrons

Now it is easy to pass over to atoms containing several electrons by introducing 6 additional variables for every further electron. The distribution function will then be

$$(41)\quad f = f(x_1, y_1, z_1, \dot{x}_1, \dot{y}_1, \dot{z}_1, \ldots x_N, y_N, z_N, \dot{x}_N, \dot{y}_N, \dot{z}_N) ,$$

if N is the number of electrons per atom. Then equations (1), (4), and (5) have to be modified in accordance with the number of additional variables, and we have to take into consideration the

mutual interaction of the electrons within the atoms. The result will be Schrödinger's time-independent equation (4o) with

$$(42)\quad H = \sum_{k=1}^{N} \left[-\frac{\kappa^2}{2m_k} \nabla_k^2 + V(x_k, y_k, z_k) \right] + \sum_{k+j=1}^{N} V_{kj}(x_k, y_k, z_k, x_j, y_j, z_j)$$

and

$$(43)\quad \nabla_k^2 = \frac{\partial^2}{\partial x_k^2} + \frac{\partial^2}{\partial y_k^2} + \frac{\partial^2}{\partial z_k^2}$$

Incidentally, we obtain the same result, if the electrons within the atoms are supposed to be indistinguishable. Then the number of permutations (1) has to be divided by the constant factor N!.

The transition to the squares of the amplitudes

As early as 1931 Schrödinger himself raised the following objection against the possibility of deriving wave-mechanics from statistical mechanics. Pointing out their mutual discrepancies he wrote[11]:

"The first one is that in the classical theory of statistical systems ("Zufallssysteme") the density of probability itself is subject to a linear differential equation, whereas in wave-mechanics it is the so-called amplitude of probability, from which all probabilities are made up bilinearly."

Indeed, the time-independent Schrödinger equation (38) presents a special difficulty. In general there are negative solutions. However, electron numbers or probabilities are positive quantities. Therefore, usual presentations of quantum theory pass over to the squares of the amplitudes pointing to the fact that the results of the calculations agree with ob-

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11) see footnote 7).

servations. This reasoning would be acceptable, if proof could be given that ψ^2 is a solution of the problem as well. It is an advantage of the statistical method applied above that this proof can in fact be given here.

Let us assume that ψ is a solution of Schrödinger's equation (38). Then it is possible to show that ψ^μ (μ real > 0) obeys the following equation

$$(44)\qquad V\psi^\mu - \frac{\kappa^2}{2m}\,\frac{1}{\mu}\left(\frac{\partial^2\psi^\mu}{\partial x^2}+\frac{\partial^2\psi^\mu}{\partial y^2}+\frac{\partial^2\psi^\mu}{\partial z^2}\right) = E\psi^\mu .$$

Proof:

$$(45)\qquad \frac{\partial^2\psi^\mu}{\partial x^2} = \mu\psi^{\mu-1}\frac{\partial^2\psi}{\partial x^2} + \mu(\mu-1)\psi^{\mu-2}\left(\frac{\partial\psi}{\partial x}\right)^2$$

and

$$(46)\qquad \frac{\partial^2\psi^\mu}{\partial x^2}+\frac{\partial^2\psi^\mu}{\partial y^2}+\frac{\partial^2\psi^\mu}{\partial z^2} = \mu\psi^{\mu-1}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right) + \mu(\mu-1)\psi^{\mu-2}\,|\mathrm{grad}\,\psi|^2 .$$

Now,

$$(47)\qquad \frac{\partial\psi}{\partial x} = 0 \quad ,$$

since equation (29) yields

$$(48)\qquad \frac{\partial\psi}{\partial x} = 0$$

Hence

$$(49)\qquad \frac{\partial^2\psi^\mu}{\partial x^2}+\frac{\partial^2\psi^\mu}{\partial y^2}+\frac{\partial^2\psi^\mu}{\partial z^2} = \mu\psi^{\mu-1}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right).$$

Thus equation (44) transforms itself into

$$(50)\qquad V\psi^\mu - \frac{\kappa^2}{2m}\,\psi^{\mu-1}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right) = E\psi^\mu .$$

Division by $\psi^{\mu-1}$ finally leads to equation (38). Of course, the direction of the proof given above might also be reversed. Then equation (44) turns out to be a consequence of equation (38).

The theory does not give any information about the constant K appearing in equation (38). Its value has to be determined by experiment. The fact that calculations agree with observations, if

(51) $$K = \hbar$$

and

(52) $$\mu = 2 \quad ,$$

obviously means that the fundamental equation for the probability distribution is

(53) $$V\psi^2 - \frac{\hbar^2}{2m}\,\frac{1}{2}\left(\frac{\partial^2\psi^2}{\partial x^2} + \frac{\partial^2\psi^2}{\partial y^2} + \frac{\partial^2\psi^2}{\partial z^2}\right) = E\psi^2 .$$

It is noteworthy that the constant appearing in this equation is $\hbar^2/2$ in place of $\hbar^2$. However, since according to the considerations given above, equation (53) can be transformed into the time-independent Schrödinger equation

(54) $$V\psi - \frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = E\psi \, ,$$

Schrödinger's objections against a statistical derivation of equation (54) cannot be maintained any longer.

Schrödinger's time-dependent equation

Let us now assume that after a period in which the system is in the stationary state, disturbing time-dependent forces will affect all particles in the same way. As an approach to the non-stationary problem we first calculate the variation of density in phase space to be expected in the stationary case on account of equation (7):

(55) $f = f(x, y, z, \dot{x}, \dot{y}, \dot{z}, t) = A e^{-\alpha [V(x,y,z,t) + \frac{m}{2}(\dot{x}^2+\dot{y}^2+\dot{z}^2)]}$.

Then the variation $\Delta f_{st.}$ of the original density is

(56) $\Delta f_{st.} = f - f_0 = A\left(e^{-\alpha E(t)} - e^{-\alpha E_0}\right)$

or approximately

(57) $\Delta f_{st.} = -\alpha f [E(t) - E_0] = -\alpha f \Delta E$,

provided that

(58) $\frac{\Delta E}{E_0} \ll 1$.

Next, we introduce the following assumption:

The variation of density df, caused by varying forces, is proportional to the stationary variation $\Delta f_{st.}$ multiplied by the increment in time dt; i.e.

(59) $df = q \Delta f_{st.}\, dt = -q\alpha f (E(t) - E_0)\, dt$; $q = const.$

Hence

(60) $\frac{\partial f}{\partial t} = -q\alpha f (E(t) - E_0)$

or

(61) $\frac{\partial f}{\partial t} = -\beta f (E(t) - E_0)$

with

(62) $\beta = q\alpha$.

It may be remarked here that the statistical assumption (59) corresponds to Ilya Prigogine's principle of local equilibrium applied in non-equilibrium thermodynamics[13].

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13) Ilya Prigogine, Zeit, Struktur und Fluktuationen.: In: Angewandte Chemie, 90. Jg, 1978, p. 704-715.

According to the considerations which led to the time-independent Schrödinger equation, we apply equation (31) on E(t)f(t), so that

$$(63)\quad \frac{\partial f}{\partial t} = -\beta\left[f V - \frac{\kappa^2}{2m}\left(\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \right) \right] + \beta E_0 f .$$

Again we obtain the same distribution in geometrical space for all independent variables in velocity space. Therefore the substitution

$$(64)\quad f(x, y, z, \dot{x}, \dot{y}) \rightarrow \psi(x, y, z)$$

yields

$$(65)\quad \frac{\partial \psi}{\partial t} = -\beta \left(H(t) - E_0 \right) \psi$$

in complete analogy to the calculation of the time-independent Schrödinger equation.

From equation (65) we conclude: If the potential function does not vary in time and if the time-independent Schrödinger equation is valid, then the density of probability does not vary either. If, on the other hand, potential and density function do not vary in time, then the time-independent Schrödinger equation is valid. Therefore, equation (65) is in accordance with the stationary result.

Now, the potential V in the Hamilton operator H contains an arbitrary additive term C. If we put

$$(66)\quad C - E_0 ,$$

then

$$(67)\quad \frac{\partial \psi}{\partial t} = -\beta H \psi .$$

Here the potential constant has vanished from the Hamilton operator.

The same consideration may be applied to any stationary state E_0. Of course, the potential constant then assumes different values in different cases. However, since C is arbitrary, equation (67) comprehends all stationary states.

So far β is assumed to be a real number $\neq 0$. Consequently, there is a variation of the ψ-function in time, since $H\psi \neq 0$. If, on the other hand,

$$\frac{\partial \psi}{\partial t} = 0 \quad , \tag{68}$$

we obtain

$$H\psi = 0 \tag{69}$$

in place of the time-independent Schrödinger equation.

Yet, we must expect that by the foregoing considerations touching the potential constant, the fundamental property of our theory, namely its transition into the time-independent Schrödinger equation in any case in which the potential function does not vary in time, will not be lost.

Therefore, if we assume that the time-dependence of the ψ-function is

$$\psi = f(t)\,\psi(x,y,z) \quad , \tag{70}$$

equation (67) yields

$$-\frac{1}{\beta}\,\frac{f'(t)}{f(t)}\,\psi(x,y,z) = H\psi(x,y,z) \, . \tag{71}$$

Since we want to preserve the time-independent Schrödinger equation,

$$-\frac{1}{\beta}\,\frac{f'(t)}{f(t)} = E \tag{72}$$

or

$$f(t) = e^{-\beta E t} \, . \tag{73}$$

Yet, the time dependent factor (73), in combination with (7o), does not yield the stationary ψ -function, in accordance with our considerations concerning equation (67).

Therefore we are compelled to admit complex values of the ψ -function by introducing a complex constant in equation (59):

(74) $$\beta_c = \delta + i\gamma \quad ; \quad \delta, \gamma \text{ real.}$$

Then equation (67) reads

(75) $$\frac{\partial \psi_c}{\partial t} = -\beta_c H \psi_c \quad .$$

The assumption (7o) leads to

(76) $$\psi_c = e^{-(\delta + i\gamma) E t} \psi(x, y, z).$$

This yields the result of the time-independent Schrödinger equation, if we take the absolute amount and if

(77) $$\delta = 0 \quad .$$

Moreover, the theory agrees with experiments, if

(78) $$|\beta_c| = |\gamma| = \frac{1}{\hbar} \quad .$$

Therefore, from equations (74), (75), and (78) we finally obtain the time-dependent Schrödinger equations

(79) $$i\hbar \frac{\partial \psi}{\partial t} = H \psi$$

and

(8o) $$-i\hbar \frac{\partial \psi}{\partial t} = H \psi \quad .$$

Concluding remarks

The deduction of wave-mechanics given here seems to have some advantages over other methods of introducing Schrödinger's equations. First of all, our attempt takes away the mystical aura common to many axiomatic presentations of wave-mechanics. Secondly, we reply to all questions raised in the introductory chapter. Thirdly, Schrödinger's theory is here deduced from two simple assumptions, the first of which was already at the bottom of Boltzmann's statistical researches. Thus, the intimate genetic and systematic connections between Boltzmann's entropy theorem and Schrödinger's wave-mechanics become apparent, when viewed in this light. Therefore, we may say that Boltzmann was a true forerunner of wave-mechanics which seems to be nothing else than a consistent development of Boltzmann's statistics.

Moreover, we dispense with the heuristically valuable, but often criticized wave interpretation of matter, and therefore dismiss duality and complementarity. Our theory is corpuscular and statistical from the beginning. There is no need for an a posteriori statistical interpretation of the ψ-function or for non-classical atom-mechanics like Heisenberg's matrix-mechanics.

In addition we offer theoretical reasons for the transition to the squares of the amplitudes in the theory of Schrödinger's time-independent equation, and to the squares of the absolute amounts in the theory of the time-dependent equation, while these transitions are usually made ad hoc to fit the experiments.

Finally it should be remembered that Heisenberg's uncertainty relations do not play any part in our deduction. This provides evidence in support of Popper's early criticism of quantum theory, namely that Heisenberg's uncertainty relations (for coordinates and moments) do not represent a property of atomic particles or of our measuring devices, but are scatter relations[12] which seem to be intimately connected with Liouville's theorem of classical mechanics.

12) Karl R. Popper, Logik der Forschung. 2nd ed., Tübingen 1966, p. 167.

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